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Request for grant of a patent

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1. Your reference — RJG/VC/4237 GB

2. Patent application number *(The Patent Office will fill in this part)* — 0329728.0

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

University of Brighton
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Patents ADP number *(if you know it)* — 788741300 2

If the applicant is a corporate body, give the country/state of its incorporation — United Kingdom

(See attached sheet for co-applicants)

4. Title of the invention — ELECTRODE FOR USE IN ELECTROCHEMICAL SENSOR

5. Name of your agent *(if you have one)* — STEVENS HEWLETT & PERKINS

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

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EC1N 2JD

Patents ADP number *(if you know it)* — 1545003

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:* — YES

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

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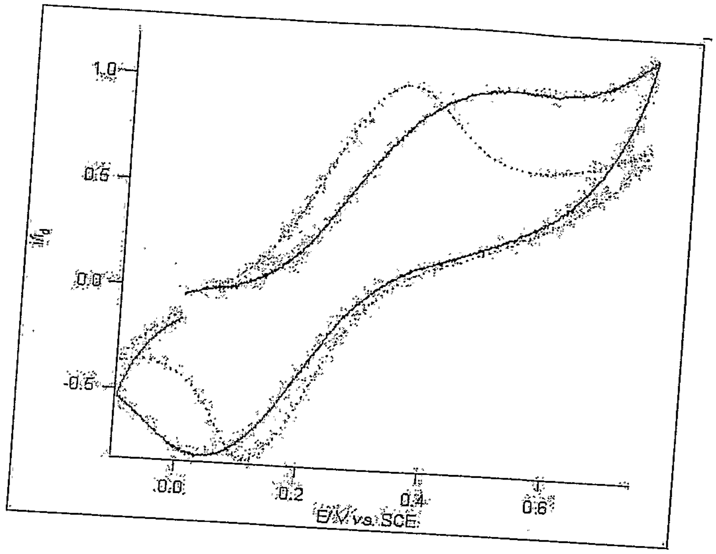


Figure 1

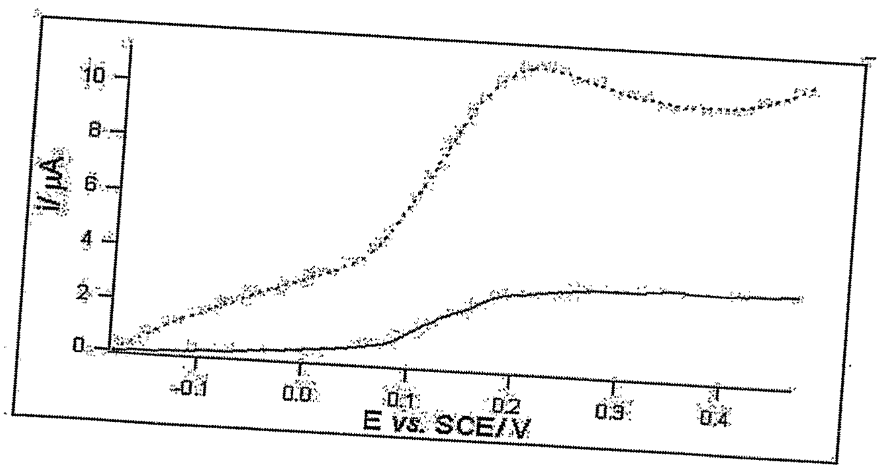


Figure 2

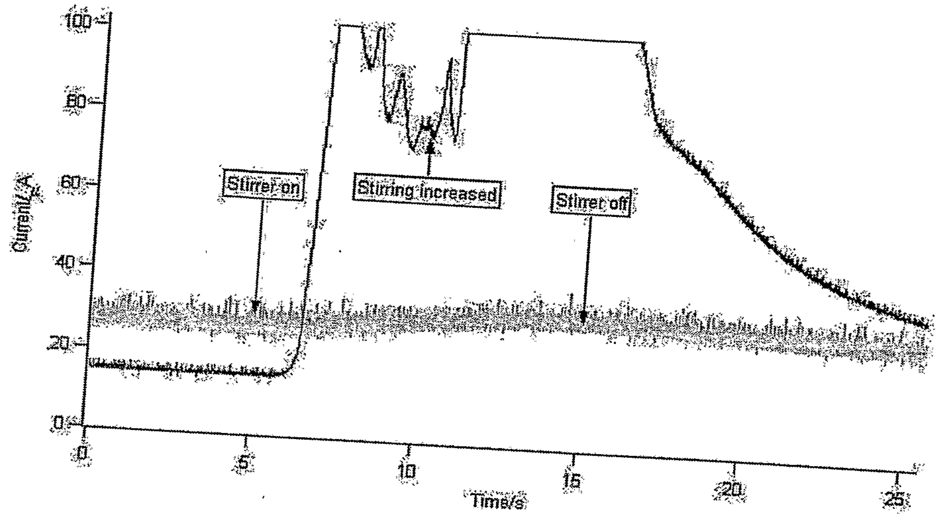


Figure 3

Composition	Area fraction found by C-AFM	Predicted slope of Levich plot/ A (rad $s^{-1})^{-1/2}$	Experimental slope of Levich plot/ A (rad $s^{-1})^{-1/2}$	∴ Area fraction comparable boundary layer
Bulk conductor	1	1.61×10^{-5}	1.61×10^{-5}	-
40% (w/w)	0.25	4.02×10^{-6}	1.28×10^{-6}	0.318
50% (w/w)	0.33	5.31×10^{-6}	1.30×10^{-6}	0.244
60% (w/w)	0.63	1.01×10^{-5}	8.20×10^{-6}	0.81

Figure 4

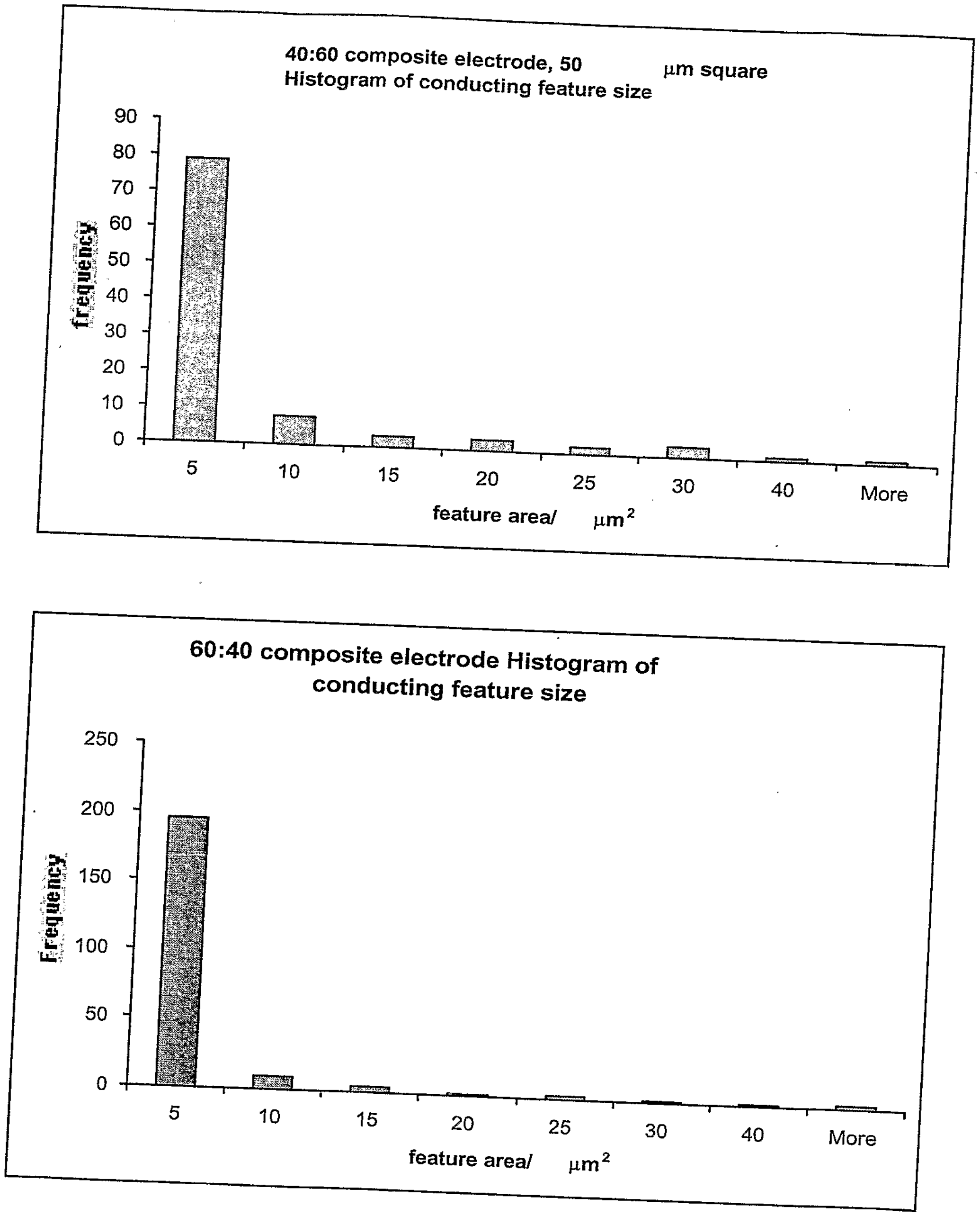

40:60 composite electrode, 50 µm square
Histogram of conducting feature size
frequency
90
80
70
60
50
40
30
20
10
0
5
10
15
20
25
30
40
More
feature area/ µm²
60:40 composite electrode Histogram of conducting feature size
Frequency
250
200
150
100
50
0
5
10
15
20
25
30
40
More
feature area/ µm²

Figure 5

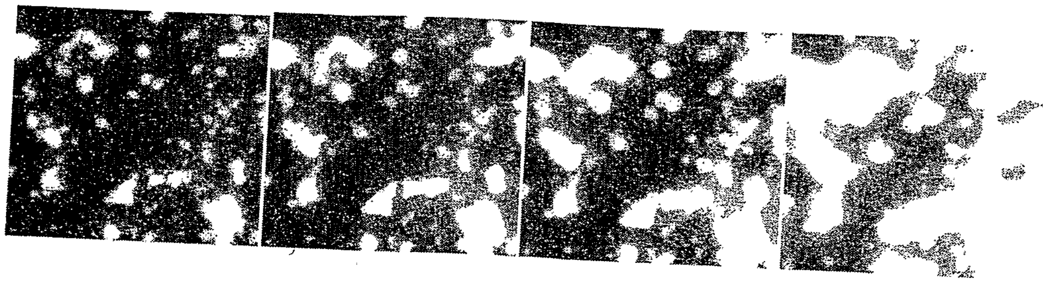


Figure 6

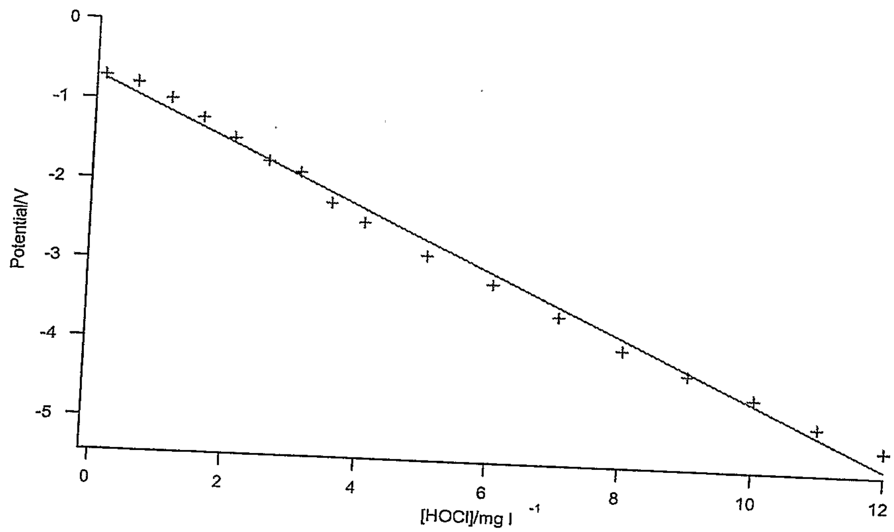


Figure 7

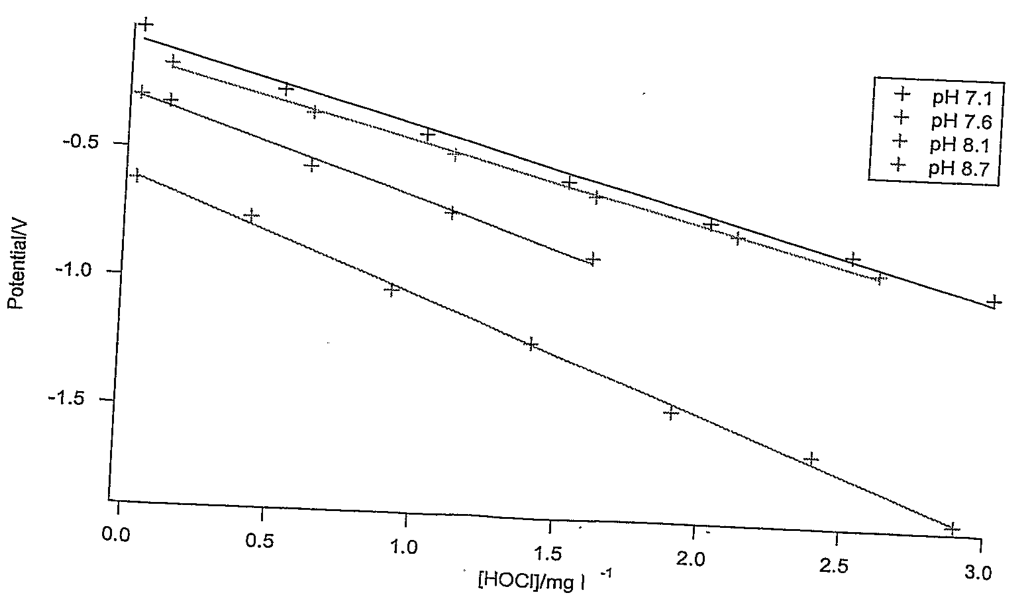
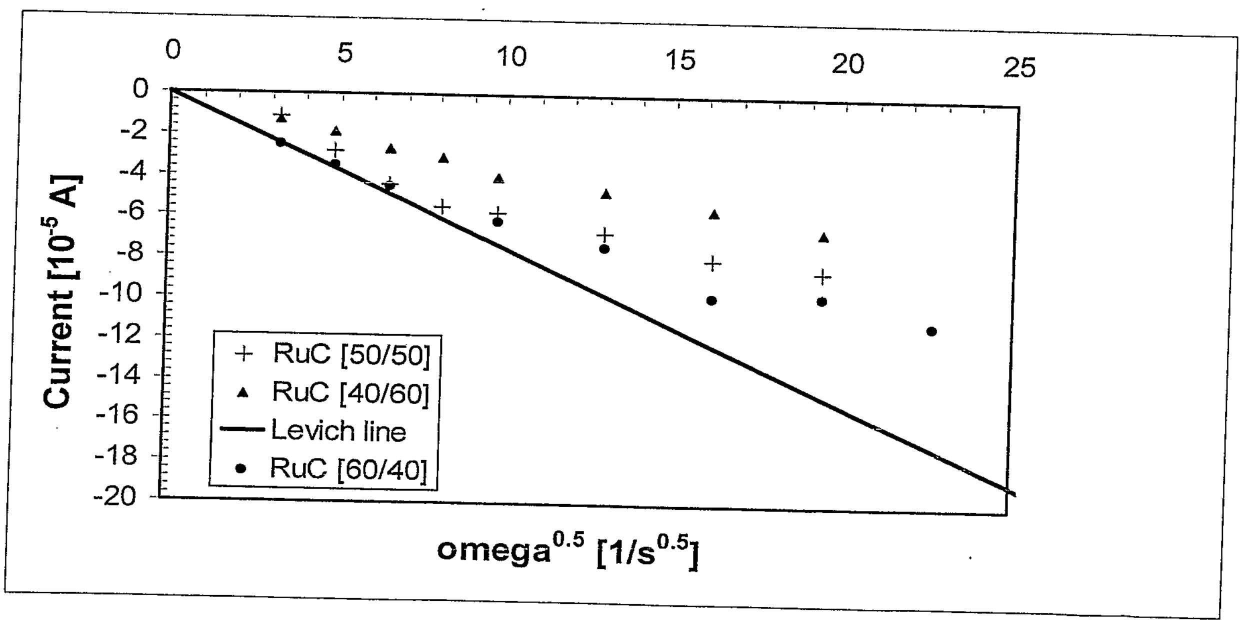


Figure 8

Figure 9


0
5
10
15
20
25
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
Current [10^-5 A]
omega^0.5 [1/s^0.5]
RuC [50/50]
RuC [40/60]
Levich line
RuC [60/40]

Electrode for use in electrochemical sensor

The present invention relates to an electrode for use in an electrochemical cell. Particularly, but not exclusively, the present invention relates to an electrode which is made from a conducting composite material, the electrode being intended for use in an electrochemical sensor for the detection and measurement of free available chlorine.

With the increased demand for electrochemical sensors, the type of electrode used in electrochemical sensors has become the subject of much research, and is critical in achieving high performance in modern detection systems. The various types of electrodes currently in use differ from one another with respect to their composition, dimensions, electrochemical properties, cost, simplicity and range of analytes with which they are used. Electrochemical sensors are commonly used to detect chemical species in solution and as a consequence, each sensor may be designed to be specific to the chemical species to be detected.

Not all electrode geometries provide a reproducible current however, since the region immediately surrounding the electrode surface is depleted of analyte, forming what is commonly referred to as a depletion zone. Convection arising from temperature and density

variations for example, whilst reducing the depletion zone, also result in disturbance of the concentration gradient of the analyte and thus the current flowing. There are various ways of stabilising the depletion zone surrounding the electrode, including (i) forced *reproducible* convection, (ii) use of a Clark- type oxygen electrode whereby a permeable membrane is applied to the electrode, and (iii) the use of microelectrodes.

In the case of microelectrodes, due to their small size, the depletion zone around the electrode is small compared with the boundary layer due to natural convection. As a result, the rate of flux is independent of the flow conditions. In practice, for aqueous solutions at ambient temperatures, this means that microelectrodes need to have a characteristic dimension of less than 50 μm to fulfil this criteria. Accordingly, by making the electrode small, the need for the complex engineering usually associated with the forced reproducible convection required to stabilise the depletion zone, is eliminated.

Although there are significant advantages associated with the use in electrochemical sensors of the microelectrodes described above, not least the associated rapid response times, there also exists significant

disadvantages. In particular, due to their small size, low currents are generated by microelectrodes which, whilst easily manageable in a research laboratory environment, present instrumental difficulties in electromagnetically noisy measurement situations such as operating theatres and process lines where it is not always necessary to have a physically tiny device but where the rapid response times of microelectrodes and their relative insensitivity to convective flow are nonetheless desirable.

One solution to the above problem is the use of *arrays* of microelectrodes in parallel in electrochemical sensors. Microelectrode arrays advantageously exhibit low dependence of current on convective flow, show enhanced rates of diffusive mass transport, and have rapid response times, whilst producing an easily manageable current in realistic situations.

However, microelectrode arrays, although regularly described in research literature, are in practice expensive to manufacture, relying either on high levels of expertise in their construction, or capital intensive C-MOS manufacturing techniques (semi-conductor fabrication technology). Although the latter technique is a useful method of microelectrode array manufacture, it (i) suffers from poor design flexibility in that a new mask is required each time the design of the microelectrode array is fine tuned, and (ii) is restricted to planar geometry and materials which are often unsuitable

for application in electrochemical sensors due to hydration, ion exchange or poor biocompatibility.

It has however, been noted for some time that composite electrodes made from conducting particles embedded in an insulating binder can behave in a similar way to microelectrode arrays. The use of such composite electrodes is considerably cheaper than the use of microelectrode arrays, and does not suffer from the manufacturing disadvantages of microelectrodes discussed above. In addition, the modification of both the conducting particles of the electrode and the insulating matrix by catalysts, enzymes, redox mediators or other elements conferring (i) selectivity (ii) improved electrode reaction kinetics (iii) improved biocompatibility and resistance to fouling (iv) reagents including but not restricted to drugs and/or biocides, is considerably easier.

Although the use of conducting composite materials as electrodes in electrochemical sensors has been the subject of much research, as far as the inventor is aware, emphasis to date has been mainly on maximising the bulk conductivity of such composite electrodes, and many experiments have been performed to increase knowledge of the relationship between the composition of the electrodes and their conductivity. In maximising the bulk conductivity of the electrodes, conventional electrochemical tools may be employed for their characterisation, and off-the-shelf electrochemical

instrumentation may be used with sensors based on such materials. Furthermore, highly conductive composite electrodes minimise the Ohmic iR drop within the electrode, which in turn simplifies both data analysis and implementation in sensors. Further still, the reactance (for instance, as measure by the RC time constant) of such electrodes is minimised if the conductivity is maximised.

As well as possessing the advantages associated with low electrical resistance as detailed above, highly conductive composite electrodes are relatively easy to characterise using accepted models and as a result, research on composite electrodes to date has emphasised the need for negligible resistance.

To date however, there has been little consideration of the relationship between the composition of the electrodes and their electrochemical properties, such as their microelectrode array-like behaviour.

Microelectrode array-like behaviour can be investigated by means of voltammetric techniques, principally steady state methods, and observation of the conducting features of the composite. The fraction of the surface area that is conducting and the size of the conducting features have been quantified using the technique of conducting atomic force microscopy (C-AFM), and this has helped to show the relationship between composition of

the electrode and the microelectrode array behaviour thereof.

In his paper "On the microelectrode behaviour of graphite-epoxy composite electrodes" Electrochemistry Communications 4 (2002) 245 – 250, the inventor has previously investigated the behaviour of carbon-epoxy composites, which were made in the carbon to epoxy mass ratios 40:60, 50:50 and 60:40, using C-AFM. The equivalent volume ratios are 25:75, 33:67 and 63:37, respectively. The blends covered the concentration range from just above the lower percolation limit to just up to the second percolation limit. Percolation theory is mentioned herein, and is a specific type of graph theory used to model the behaviour of materials. However, it is to be noted that there are alternative, non-graph theoretical ways of describing these materials. The lower percolation limit is the value of the conducting fraction of the composite at which conduction rises sharply; that is, the point at which the insulator to conductor transition takes place. The second percolation limit is the value of the conducting fraction at which the insulating phase is no longer continuous.

Using C-AFM, both the 50:50 and 40:60 samples have been shown to possess conducting features with a wide variety of size, shapes and spacing, but to have many features of an appropriate size and spacing to account for microelectrode array like behaviour. Since diffusion-limited current density is substantially higher for microelectrodes, this ensures that

the voltammetric behaviour is dominated by these smaller features (vide infra, the rotating disc experiments).

Microelectrode behaviour of the carbon-epoxy composite electrodes has been further confirmed using voltammetry. Cyclic voltammograms typical of microelectrodes were achieved for 60:40 (dotted line) and 50:50 (solid line) carbon-epoxy composite electrodes at 100 mVs^{-1} in 1 mol m^{-3} $K_4Fe(CN)_6$ with 100 mol m^{-3} aqueous KCl. To enable comparison, the currents were normalised to the mass transport limited anodic current. Qualitatively, it is apparent that the 50:50 electrode shows a sigmoidal current voltage curve on the rising part of the voltammogram, which again, is consistent with microelectrode behaviour.

Although the carbon-epoxy electrode described above exhibits notable microelectrode array-like behaviour, carbon-epoxy composites show little or no response to dissolved chlorine. Where there is a response to change in free available chlorine concentration however, sensitivity (i.e.current per unit change in concentration) is irreproducible.

There exists a need to provide an improved electrode which exhibits the advantageous effects of a microelectrode array, whilst avoiding at least the above-mentioned disadvantages associated therewith. There further exists a need to provide an electrode which provides improved detection of free

available chlorine.

Free available chlorine is defined in “Chemical Disinfecting Agents in Water and Effluents, and Chlorine Demand” No. 27 in the series “Methods for the Examination of Waste Water and Related Materials” published by the Department of the Environment, HMSO, 1980, isbn 0117514934.

The present invention is based on the finding that electrodes having a particular composition surprisingly show improved microelectrode array-like behaviour, in particular in the detection of free available chlorine.

In accordance with a first aspect of the present invention there is provided an electrode for use in the detection of free available chlorine, comprised of a metallised carbon-epoxy composite.

In accordance with a second aspect of the present invention there is provided a method for the manufacture of an electrode comprising the steps of formulating a metallised carbon-epoxy composite. The composite can be formulated using the techniques described in the experimental account that follows.

In accordance with a third aspect of the present invention there is provided a free available chlorine sensor comprising an electrode made from a metallised carbon-epoxy composite.

The metallised particles of the composite electrode advantageously catalyse the electro-chemical reduction of free available chlorine.

The inventor has found that microelectrode behaviour becomes less apparent close to or above the second percolation threshold. As discussed in his paper "On the Microelectrode behaviour of graphite epoxy composite electrodes" Electrochemistry Communications 4 (2002) 245 – 250, all electrochemical sensors to date are based upon conducting composite materials having a high conducting fraction such that they are close to or above the second percolation threshold. However, metallised carbon epoxy composite electrodes of the present invention have compositions above but close to the lower percolation threshold. Electrode compositions above but close to the lower percolation threshold of bulk conductivity are characterised by a large number of widely-spaced microscopic conducting features which leads to the microelectrode array-like behaviour.

The inventor has found that electrode formulation is based on the volume fraction, as opposed to the mass fraction. The volume fraction is substantially identical to the area fraction for randomly dispersed particles.

Metallised carbon-epoxy composite electrodes exhibit low sensitivity to flow and are resistant to fouling. Such advantageous characteristics significantly increase the utility of sensors using this type of electrode especially where the matrix is characterised by poorly defined or time-varying convection (blood and non-Newtonian fluids generally, physiological applications, process control, food processing, and environmental monitoring). Furthermore, sensors using this type of electrode are particularly useful where the medium is poorly conducting, and where there are surface active constituents in the matrix (physiological preparations, cell and tissue culture, and biological and environmental samples).

In using metallised carbon-epoxy composites, the sensitivity (current per unit change in concentration) and linear range can be tuned through varying the metal or catalyst content and identity. Further, selectivity is affected by both metal or catalyst concentration and identity, and so can be altered.

It is preferred, but by no means essential that the electrode is made from a ruthenium modified carbon catalyst epoxy composite. Ruthenium modified carbon catalyst immobilised in low concentration in epoxy resin matrix has shown excellent ability to measure dissolved chlorine, hypochlorite and hypochlorous acid in swimming pool water with good selectivity in the

presence of chloramines, high total organic carbon and over a wide range of pH values. The device is stable despite immersion and intermittent use over several months at least.

Alternatively, the electrode may be made from a platinum modified carbon catalyst epoxy composite, or a rhodium modified carbon catalyst epoxy composite. It is to be understood however, that other suitable metallised carbon epoxy composites may also be used in the detection of free available chlorine.

Metallised carbon epoxy composite materials such as those disclosed above can be extruded, moulded, printed or machined into a suitable form ranging in size from sub-millimetre, i.e. around 10μm, to several centimetres dimensions.

The electrodes made from such composites can be used singly, or alternatively several may be used in parallel. In the case where several composite electrodes are used in parallel, elements with similar selectivities may be used, or alternatively, electrodes with differing selectivities may be used, thereby producing sensors applicable to various different analytes.

The present invention will now be described, by way of example only, with reference to the accompanying example and drawings in which: -

Figure 1 shows sigmoidal current voltage curves for various non-metallised composite electrodes.

Figure 2 shows current voltage curves for non-metallised composite electrodes having a more dilute formulation than those of Figure 1.

Figure 3 shows the response to stirring of a 60% (w/w) carbon epoxy composite electrode compared with a glassy carbon electrode.

Figure 4 is a table showing the sensitivity to flow of various non-metallised composite electrode compositions.

Figure 5 shows histograms of the conducting feature size distribution in various non-metallised composite electrodes.

Figure 6 shows confocal fluorescence imaging of the electrode reaction as the potential increases.

Figure 7 shows simulated field conditions testing using a 40:60 Carbon and Ruthenium composite electrode. Typical calibration curve measured at pH 7.1, concentrations measured against standard DPD test.

Figure 8 shows simulated field conditions testing using a 40:60 Carbon and

Ruthenium composite electrode. Calibration curves measured at various pH, concentrations measured against standard DPD test.

Figure 9 is a graph showing the dependence of the diffusion limited current on the square root of the rotation rate.

Example

Metallised carbon epoxy composites were manufactured in the following manner: -

Low viscosity epoxy resin ('Araldite' CY1300+HY1301 Ciba-Geigy, Duxford, Cambs. U.K.) was prepared according to the manufacturer's schedule and degassed under vacuum. It was then mixed with ruthenium- or ruthenium platinum-modified carbon (metal content in the range 0.5 to 10% by weight) in the ratios of 22% to 45% by volume. The mixture was degassed under vacuum prior to casting. The electrodes may be inlaid discs made by casting the composite into an insulating electrode body, or conducting discs made by sectioning cast and cured composite and mounting them into an electrode, for example. For the latter, the composite was packed into plastic tubes (typically 7 mm diameter). After setting and curing according to the manufacturer's schedules, the resulting composites were sectioned with a precision diamond saw (Buehler Isomet) into 1 mm and 2

mm slices. The slices were mounted on an insulating tube and electrical contact made either using silver loaded epoxy composite or a spring. It is to be noted that the metallised carbon epoxy composites are not restricted to discs or even to an inlaid arbitrary shape since the devices still work when cast in a fairly haphazard way. The devices are only cut into a flat shape to aid analysis of their performance. The composite material can make satisfactory electrodes by printing or painting.

In Figures 1 to 6, it is shown that the microelectrode-like behaviour of the non-metallised composite electrode depends strongly on composition through the combination of voltammetry and conducting probe atomic force microscopy (C-AFM). This latter technique generates images of the surface conductivity and the conducting feature size and distribution has been measured down to sub-micrometre length scale. Significant microelectrode behaviour, notably the relative insensitivity to convective flow, compared with bulk conductors and highly concentrated dispersions is observed.

Tips for the rotated disc experiments (described below) were machined out of PVC, abraded lightly with 2500 grit emery paper, and rinsed in ethanol. Self adhesive copper tape was punched out and applied as a backing for the composite. The recesses (typically 2 mm) were filled with carbon epoxy composite and allowed to cure. The top 0.5 mm was removed with a

precision diamond wafering saw. The surfaces were polished with successively finer grades of aqueous alumina slurry down to 0.05 μm. Prior to the experiments, the electrodes were cycled in sulfuric acid (100 mol m^{-3}) between the potentials of oxygen and hydrogen evolution for 10 minutes at 1 V s^{-1}, held at hydrogen evolution potential for a further 15 minutes. The electrodes were then rinsed in de-ionised water and kept wet till needed.

Voltammetric behaviour

Figure 1 shows sigmoidal current voltage curves characteristic of microelectrode behaviour for the 50% (w/w) non-metallised composite electrode (solid line) and the more peak shaped response shown by the 60% (w/w) formulation (pecked line). For the more dilute formulations, this phenomenon is general over the accessible timescales (dictated by the RC time constant of the electrode) whereas maximally conductive composites only show this behaviour at scan rates less than 50 mV s^{-1} (see Figure 2)

Response to convection

Figure 3 compares the response to stirring of a 60% (w/w/) carbon epoxy composite electrode with a glassy carbon electrode. Even this comparatively highly conductive composite shows diminished response compared with the poorly reproducible response of a bulk conductor.

Stirring the electrochemical cell elicited no change in the steady state current for the lower concentration composites.

The convective boundary layer at a rotated disc is of uniform thickness and can be calculated from an equation due to Von Karmen in Angew. Math. Mech. 1 233 (1921). Only those conducting features which have a characteristic dimension comparable to the boundary layer thickness will contribute to the variation of current with boundary layer thickness. As the rotation speed increases, the slope of i_d *vs.* $w^{1/2}$ (the Levich plot) should increase as the boundary layer thickness decreases and ever smaller features are recruited into the flow dependent regime. It is a simple matter to calculate the expected slope of these curves for different formulations based on the measured conducting area from the C-AFM data. Image analysis of the C-AFM images allows construction of a histogram of feature areas and perimeters, *vide infra*.

3 mm radius disc electrodes were used for this study. The redox probe was ruthenium (III) chloride (1 mol m^{-3}) in KCl (1000 mol m^{-3}). Using published values of the diffusion coefficient (D = 9.1×10^{-10} m^2 s^{-1} and kinematic viscosity ($\nu = 0.00916$ cm^2 s^{-1}) the predicted slope for a bulk conducting electrode is 1.61×10^{-5} A (rad $s^{-1})^{-1/2}$. Values obtained for the various composites are summarised in Figure 4.

As is plain from the data in Figure 4, all compositions show lower sensitivity to flow than is predicted from the known measured area fractions. This is the first direct evidence that the behaviour of these devices is dominated by microscopic conducting features. This is further confirmed by the significant non-zero intercept of the Levich plots.

Non-Faradaic responses

It has been shown that for non-metallised composite materials of more typical composition, the capacitance of a polarised composite electrode in electrolyte solution (i.e. in the absence of electrolysable material) is related to the fractional surface area. This suggests that the dominant contribution is due to the electric double layer. For more dilute formulations, the capacitance scales with section thickness, showing that the dominant contribution is due to overlapping incomplete conducting pathways. In addition to providing an explanation for the large time constants observed with dilute conducting composites, this provides direct evidence for a qualitative difference between formulations close to the lower percolation limit, as employed by the inventor, to devices optimised for bulk conductivity.

C-AFM data

The mean conducting fractions for formulations of carbon in epoxy are given in Figure 4. For all concentrations below 60% (w/w) there is no significant difference between the conducting area fractions found experimentally and those predicted for randomly packed materials. The higher concentrations behave differently showing evidence of clumping i.e. non-random interactions- the composite is no longer bicontinuous but contains islands of epoxy resin in a porous but continuous conducting matrix.

Histograms of the conducting feature size distribution are shown in Figure 5. The dilute formulations are dominated by features < 10 μm.

Scanning Electrochemical Microscopy

Both feedback mode and tip generation mode SECM micrographs show that the electrochemical reaction proceeds largely on microscopic isolated conducting features for the 40% (w/w) and the 50% (w/w) compositions. These conclusions were confirmed using confocal fluorescent microscopic examination of the electrode activity (see Figure 6), a relatively new technique discussed in Electrochemical Communications 4 886 (2002) by S.Cannan *et al.* From the latter data it is also evident that the finite, non-

negligible resistance of the microelectrode-like elements is important in understanding the performance of these materials. These results underline the difficulties associated with using conventional electrochemical tools-quantitative analysis of the shape of the steady-state current voltage curves is a complex function of distributed microelectrode size and varying resistance of different microelectrode elements.

Metallised carbon-epoxy composite electrodes

-Detection of free available chlorine

Ruthenium modified carbon composite electrodes show catalytic diffusion limited response to dissolved chlorine (Cl_2, HOCl and OCl^-, the exact species depending on the pH). It has been demonstrated that sensitivity is comparable to electrodes of solid platinum group metals and Pt plated carbon. Typical calibration data is shown in Figure 7.

In sharp contrast to solid platinum electrodes, the long-term stability of both background current and slope of calibration was excellent over several months.

The electrodes were tested in a field simulation environment. Calibration curves were prepared for solutions of hypochlorite at various pH and temperatures. The electrodes were tested for response to chloramine, Total Dissolved Solids (TDS), cyanuric acid, fouling and changes in bulk convective flow.

The gradient changes little with a change in pH over a range typically found in swimming pools, as is shown in Figure 8. This is an advantage in a system where the pH is likely to fluctuate.

Total Dissolved Solids (TDS) can increase the conductivity of the water and produce a false response. A sensor that responds independent of the TDS concentration is an advantage in an environment that is frequently changing. Response to TDS in the form of KCl was investigated by addition to a solution of 2 mg l^{-1} hypochlorous acid at pH 7.5. The response changes little with the additions and is within 10% of the initial response.

There was no response of the electrode to chloramine, demonstrating that only free available chlorine is measured. Water uptake of the electrode was minimal in long term tests. Field trials have shown the stability of the electrode over six months *in situ*. The electrode has shown greater stability and resistance to fouling than existing commercially available platinum sensors.

A major advantage of the low concentration formulation (i.e 40% (w/w)) is the decreased dependence of the diffusion limited current on the regime of convective flow as compared with (a) electrodes made of bulk conducting material and (b) composite electrodes where (i) the majority of conductive

features are of a size that is comparable to or larger than the convective boundary layer thickness and / or (ii) the spacing between small conducting features is one order of magnitude less than the characteristic dimension of the conducting feature. The low dependence of the diffusion limited current on the flow and the enhanced current density typically observed greatly increases the versatility of such devices in both analysis and in applications in batteries, fuel cells and electrosynthesis. For chemical analysis, the principal advantage is that highly engineered flow cells are not required, instruments for field analysis are therefore cheaper, more robust and provide more reliable data. Mathematical analyses of convective flow remain amongst the most intractable problems in engineering.

The results shown in Figure 9 show that these advantages are indeed apparent in the case of dilute (40% (w/w)) dispersions of ruthenium modified carbon particles (5% Ru) in epoxy resin which have demonstrable utility as sensors for freely available chlorine in aqueous solution. For similar dispersions of graphite in epoxy, the flow dependence is related to the conducting feature size, size distribution and spacing as measured by conducting atomic force microscopy. This relationship can be quantified by rotating disc electrode voltammetry. Experimental data for three different compositions of ruthenium modified carbon epoxy composites are shown in Figure 9. Hexaamine ruthenium (III) chloride ($Ru(NH_3)_6Cl_3$ was used as a tracer to characterise the conducting composite electrodes since it shows

thermodynamically reversible electron transfer kinetics and therefore allows geometric factors to be isolated from the chemical condition of the electrode surface, a particular problem for carbon electrodes.

Materials and Methods

Ruthenium modified carbon (5%) was obtained from Alfa, washed in acetone (AnalAR grade) in a Soxhlet, dried at 105 °C for 12 hours. Voltammetric experiments were in $Ru(NH_3)_6^{3+}$ (1 mmol dm^{-3}, Aldrich used as received) in aqueous KCl (0.5 mol dm^{-3}). The reference electrode was a commercial aqueous silver-silver chloride (100 mmol dm^{-3} KCl) and a platinum flag served as counter electrode.

Electrode bodies were custom manufactured from PVC and consisted of a 2.5 cm cylindrical mantle with 4 mm wide cylindrical recess in the centre. The Ru-C powder was mixed with degassed epoxy resin (Cib-Geigy) in three ratios: 40% (w/w) Ru-C, 50% (w/w) Ru-C, 60% (w/w) Ru-C. Each formulation was again degassed under vacuum and packed into the cylindrical recess in the PVC electrode bodies and compressed using a PTFE mandrel. After curing according to the manufacturer's schedule, the electrodes were sawn parallel to the surface using a low speed diamond

saw (Buehler) to leave a packed recess 1 mm deep. Final polishing was with 2500 grit emery paper and successively finer alumina slurries down to 0.03 μm to obtain a mirror like finish. The electrode was mounted in a rotating disc electrode assembly (PAR) and electrical connection was established with a stainless steel spring. Final cleaning was by potential cycling between the potentials for oxygen and hydrogen evolution at 1 $V\ s^{-1}$ in sulfuric acid (0.5 mol dm^{-3}) for 20 minutes followed by 15 minutes at the hydrogen evolution voltage.

Quasi-steady state voltammograms were recorded in the ruthenium hexaammine solution at 2 $mV\ s^{-1}$. Diffusion limited steady state currents were calculated from the background corrected voltammograms.

Discussion

It is clear from Figure 9 that the Levich slope for all three formulations is below that for a bulk conductor (solid line). The results for the 50% and 60% formulations are qualitatively different from the 40% (w/w) composite. Of particular significance is the lower value of the slope at speeds below 25 s^{-1}. The higher concentration composites have slopes approaching the Levich line over the same rotation speeds confirming that the isolated conducting features are more densely packed and that microelectrode array-like behaviour is more evident for the 40% concentration.

These results quantitatively confirm that more dilute formulations of Ru-C particles in epoxy resin show disproportionately lower sensitivity to convective flow than the more commonly used high conducting fraction dispersions. This is due to the small size and wide spacing of the conducting features rendering the behaviour more like a microelectrode array.

Conclusion

The totality of evidence from voltammetry, non-faradaic responses and scanning probe microscopic investigations all confirms that dilute conducting metallised carbon epoxy composites are qualitatively different in their structure and voltammetric behaviour from composites optimised for maximum conductivity. The diminished response to convection, the enhanced mass transport, ease of modification and resistance to fouling render these materials as eminently suitable for application to electrochemical chlorine sensors.

The metallised composite electrode of the present invention has numerous fields of application, most notably water treatment, food processing, sterilisation equipment, surgical sterilisation, portable field instrumentation in water treatment and waste water treatment, waste stream remediation, industrial effluent monitoring and control, and swimming pool monitoring.

Further applications of the composite electrode of the present invention beyond electrochemical sensors include fuel cells, electrolysers and electrochemical reactors.

The present invention is not limited to the particular features of the composite electrode described above. Elements of the composite electrode may be omitted or altered, and the scope of the invention is to be understood from the appended claims.